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A Theoretical Analysis of IR Spectroscopy

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Abstract – Infrared spectroscopy was used for the structure elucidation of five new compounds isolated from the oxidation of primaquine. IR spectroscopy has shown that adsorbed water is almost completely removed from ferrihydrite by evacuation at room temperature. Absorption bands at 3615 and 3430 cm^{-1} appearing thereafter are interpreted as arising from OH groups located respectively at the surface and deeper in the structure.

Infrared spectroscopy has been used to study the structure of selected vanadates including pascoite, huemulite, barnesite, hewettite, metahewettite, hummerite. Pascoite, rauvite and huemulite are examples of simple salts involving the decavanadates anion. The other minerals namely barnesite, hewettite, metahewettite and hummerite have similar layered structures to the decavanadates but are based upon $(V5O14)^{3-}$ units.

INTRODUCTION

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied.

Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples. Infrared spectrometers have been commercially available since the 1940s. At that time, the instruments relied on prisms to act as dispersive elements, but by the mid-1950s, diffraction gratings had been introduced into dispersive machines. The most significant advances in infrared spectroscopy, however, have come about as a result of the introduction of Fourier-transform spectrometers.

This type of instrument employs an interferometer and exploits the well-established mathematical process of Fourier-transformation. Fourier-transform infrared (FTIR) spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data. In addition, with constant improvements to computers, infrared spectroscopy has made further great strides.

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. In this paper, the basic ideas and definitions associated with infrared spectroscopy will be described. The vibrations of molecules will be looked at here, as these are crucial to the interpretation of infrared spectra.

Once this paper has been completed, some idea about the information to be gained from infrared spectroscopy should have been gained. The following research will aid in an understanding of how an infrared spectrometer produces a spectrum. After working through that research, it should be possible to record a spectrum and in order to do this a decision on an appropriate sampling technique needs to be made. The sampling procedure depends very much on the type of sample to be examined, for instance, whether it is a solid, liquid or gas.

This paper also outlines the various sampling techniques that are commonly available. Once the spectrum has been recorded, the information it can provide needs to be extracted. As infrared spectroscopy is now used in such a wide variety of scientific fields, some of the many applications of the technique are examined in this research.

Spectroscopy was originally the study of the interaction between radiation and matter as a function of wavelength(λ). Historically, spectroscopy referred to the use of visible light dispersed according to its wavelength, e.g. by a prism. Later the concept was expanded greatly to comprise any measurement of a quantity as a function of either wavelength or frequency. Thus, it also can refer to a response to an alternating field or varying frequency (ν). A further extension of the scope of the definition added energy (E) as a variable, once the very close relationship $E =$

hv for photons was realized (*h* is the Planck constant). A plot of the response as a function of wavelength—or more commonly frequency—is referred to as a spectrum; see also spectral lincwidth.

Spectrometry is the spectroscopic technique used to assess the concentration or amount of a given chemical (atomic, molecular, or ionic) species. In this case, the instrument that performs such measurements is a spectrometer, spectrophotometer, or spectrograph.

Spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.

Spectroscopy /spectrometry is also heavily used in astronomy and remote sensing. Most large telescopes have spectrographs, which are used either to measure the chemical composition and physical properties of astronomical objects or to measure their velocities from the Doppler shift of their spectral lines.

Infrared spectroscopy offers the possibility to measure different types of inter atomic bond vibrations at different frequencies. Especially in organic chemistry the analysis of IR absorption spectra shows what type of bonds are present in the sample. It is also an important method for analysing polymers and constituents like fillers, pigments and plasticizers.

NEAR-INFRARED SPECTROSCOPY

The near infrared NIR range, immediately beyond the visible wavelength range, is especially important for practical applications because of the much greater penetration depth of NIR radiation into the sample than in the case of mid IR spectroscopy range. This allows also large samples to be measured in each scan by NIR spectroscopy, and is currently employed for many practical applications such as: rapid grain analysis, medical diagnosis pharmaceuticals/medicines, biotechnology, genomics analysis, proteomic analysis, interactomics research, inline textile monitoring, food analysis and chemical imaging/hyperspectral imaging of intact organisms, plastics, textiles, insect detection, forensic lab application, crime detection and various military applications. Interpretation of Near-Infrared Spectra is important for chemical identification.

Near-infrared light can penetrate the human adult head to sufficient depths so as to allow functional mapping of the cerebral cortex. Cortical activity leads to haemodynamic changes associated with an increase in cerebral metabolism. These changes in tissue oxygenation associated with brain activity modulate the absorption and scattering of the NIR photons. Oxy-haemoglobin and deoxy-haemoglobin, which are the main absorbers, have different attenuation spectra. This means that multi-wavelength systems can monitor changes in such chromophore concentrations giving qualitative measures of brain activity. This is the basis of the near-infrared techniques described in this communication.

INFRARED ABSORPTIONS

For a molecule to show infrared absorptions it must possess a specific feature, i.e. an electric dipole moment of the molecule must change during the vibration. This is the *selection rule* for infrared spectroscopy. Figure 1 illustrates an example of an ‘infrared-active’ molecule, a *heteronuclear* diatomic molecule. The dipole moment of such a molecule changes as the bond expands and contracts. By comparison, an example of an ‘infrared-inactive’ molecule is a *homonuclear* diatomic molecule because its dipole moment remains zero no matter how long the bond.

An understanding of molecular symmetry and group theory is important when initially assigning infrared bands. A detailed description of such theory is beyond the scope of this book, but symmetry and group theory are discussed in detail in other texts. Fortunately, it is not necessary to work from first principles each time a new infrared spectrum is obtained.

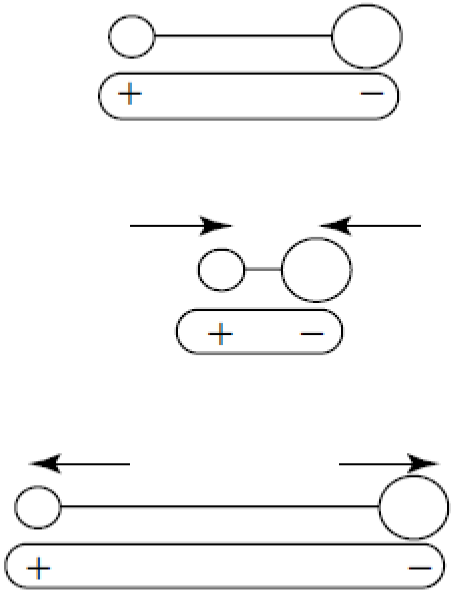

Figure 1 Change in the dipole moment of a heteronuclear diatomic molecule.

Infrared absorptions are not infinitely narrow and there are several factors that contribute to the broadening. For gases, the Doppler effect, in which radiation is shifted in frequency when the radiation source is moving towards or away from the observer, is a factor. There is also the broadening of bands due to the collisions between molecules. Another source of line broadening is the finite lifetime of the states involved in the transition. From quantum mechanics, when the Schrödinger equation is solved for a system which is changing with time, the energy states of the system do not have precisely defined energies and this leads to lifetime broadening. There is a relationship between the lifetime of an excited state and the bandwidth of the absorption band associated with the transition to the excited state, and this is a consequence of the *Heisenberg Uncertainty Principle*. This relationship demonstrates that the shorter the lifetime of a state, then the less well defined is its energy.

IR SPECTROSCOPY OF FERRIHYDRITE

Naturally occurring ferric hydroxide gel has been studied by Chukhrov *et al.* (1971, 1972, 1973) using X-ray diffraction (XRD) and infrared (IR) spectroscopy. They proposed the name ferrihydrite and concluded that it had a defect-hematite structure, as proposed earlier by Towe & Bradley (1967) for a synthetic specimen. This structure was sustained by the failure of the latter authors to detect absorption bands assignable to deformation vibrations of structural OH groups in IR spectra. Schwertmann & Fischer (1973) arrived at a similar conclusion from IR spectra of naturally occurring ferric hydroxides. Chukhrov *et al.* (1971) further stated that the presence of OH groups was precluded by the typical bonding between Fe octahedra in this type of structure. Thus on the basis of characterization by XRD, DTA and IR spectroscopy, ferrihydrite was accepted as a distinct mineral species of formula $5Fe_2O_3.9H_2O$, containing no structural OH groups (Fleischer *et al.,* 1975). The IR results quoted by these authors are central to the elucidation of the structure of ferrihydrite, but the procedures employed all involved the use of K Br pressed disks. It is suggested that this may not have been the most appropriate technique, and in this study, the spectrum of a synthetic ferrihydrite is re-examined using a film technique in conjunction with D_2O exchange.

SPECTRAL ANALYSIS

Once an infrared spectrum has been recorded, the next stage of this experimental technique is interpretation. Fortunately, spectrum interpretation is simplified by the fact that the bands that appear can usually be assigned to particular parts of a molecule, producing what are known as *group frequencies*. The types of molecular motions responsible for infrared bands in the near-infrared and far-infrared regions are also introduced.

Quantitative infrared spectroscopy can provide certain advantages over other analytical techniques. This approach may be used for the analysis of one component of a mixture, especially when the compounds in the mixture are alike chemically or have very similar physical properties (for example, structural isomers). In these instances, analysis using ultraviolet/visible spectroscopy, for instance, is difficult because the spectra of the components will be nearly identical.

Chromatographic analysis may be of limited use because separation, of say isomers, is difficult to achieve. The infrared spectra of isomers are usually quite different in the *fingerprint* region. Another advantage of the infrared technique is that it can be non-destructive and requires a relatively small amount of sample.

1. GROUP FREQUENCIES:

Mid-Infrared Region- The mid-infrared spectrum (4000–400 cm^{-1}) can be approximately divided into four regions and the nature of a group frequency may generally be determined by the region in which it is located. The regions are generalized as follows: the X–H stretching region (4000–2500 cm^{-1}), the triple-bond region (2500–2000 cm^{-1}), the double-bond region (2000–1500 cm^{-1}) and the fingerprint region (1500–600 cm^{-1}).

The fundamental vibrations in the 4000–2500 cm−1 region are generally due to O–H, C–H and N–H stretching. O–H stretching produces a broad band that occurs in the range 3700–3600 cm^{-1}. By comparison, N–H stretching is usually observed between 3400 and 3300 cm−1. This absorption is generally much sharper than O–H stretching and may, therefore, be differentiated. C–H stretching bands from aliphatic compounds occur in the range 3000–2850 cm^{-1}. If the C–H bond is adjacent to a double bond or aromatic ring, the C–H stretching wavenumber increases and absorbs between 3100 and 3000 cm^{-1}.

Near-Infrared Region - The absorptions observed in the near-infrared region (13 000–4000 cm^{-1}) are overtones or combinations of the fundamental stretching bands which occur in the 3000–1700 cm^{-1} region. The bands involved are usually due to C–H, N–H or O–H stretching. The resulting bands in the near infrared are usually weak in intensity and the intensity generally decreases by a factor of 10 from one overtone to the next. The bands in the near infrared are often overlapped, making them less useful than the mid-infrared region for qualitative analysis.

However, there are important differences between the near-infrared positions of different functional groups and these differences can often be exploited for quantitative analysis.

Far-Infrared Region- The far-infrared region is defined as the region between 400 and 100 cm^{-1}. This region is more limited than the mid infrared for spectra–structure correlations, but does provide information regarding the vibrations of molecules containing heavy atoms, molecular skeleton vibrations, molecular torsions and crystal lattice vibrations. Intramolecular stretching modes involving heavy atoms can be helpful for characterizing compounds containing halogen atoms, organometallic compounds and inorganic compounds. Skeletal bending modes involving an entire molecule occur in the far infrared for molecules containing heavier atoms because bending modes are usually no more than one-half of the wavenumber of the corresponding stretching mode. Torsional modes arise because the rotation about single bonds is not ‘free’. As a result, when certain small groups are bonded to a large group, they undergo a motion with respect to the heavier ‘anchor’ group. Crystal lattice vibrations are associated with the movement of whole molecular chains with respect to each other in crystalline solids.

2. IDENTIFICATION:

There are a few general rules that can be used when using a mid-infrared spectrum for the determination of a molecular structure. The following is a suggested strategy for spectrum interpretation:

1. Look first at the high-wavenumber end of the spectrum (>1500 cm^{-1}) and concentrate initially on the major bands.

2. For each band, ‘short-list’ the possibilities by using a correlation chart.

3. Use the lower-wavenumber end of the spectrum for the confirmation or elaboration of possible structural elements.

4. Do not expect to be able to assign every band in the spectrum.

5. Keep ‘cross-checking’ wherever possible. For example, an aldehyde should absorb near 1730 cm^{-1} and in the region 2900–2700 cm^{-1}.

6. Exploit negative evidence as well as positive evidence. For example, if there is no band in the 1850–1600 cm^{-1} region, it is most unlikely that a carbonyl group is present.

7. Band intensities should be treated with some caution. Under certain circumstances, they may vary considerably for the same group.

3. HYDROGEN BONDING:

The presence of hydrogen bonding is of great importance in a range of molecules. For instance, the biological activity of deoxyribonucleic acid (DNA) relies on this type of bonding. Hydrogen bonding is defined as the attraction that occurs between a highly electronegative atom carrying a non-bonded electron pair (such as fluorine, oxygen or nitrogen) and a hydrogen atom, itself bonded to a small highly electronegative atom. An example of this type of bonding is illustrated by the interactions between water molecules in Figure 2. This is an example of *intermolecular* hydrogen bonding. It is also possible for a hydrogen bond to form between appropriate groups within the one molecule. This is known as *intramolecular* hydrogen bonding and is illustrated by the protein structure shown in Figure 3. The segments shown belong to the same protein molecule.

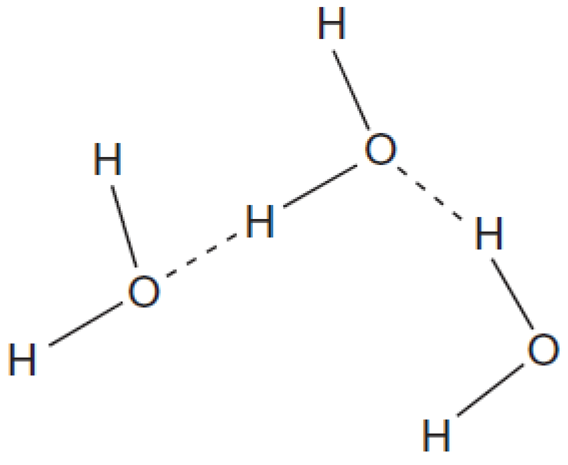

Figure 2 Hydrogen bonding of water molecules.

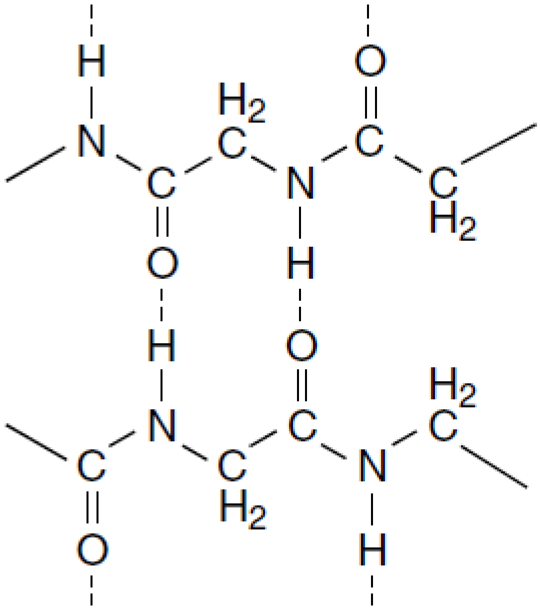

Figure 3. Intramolecular hydrogen bonding in a protein.

Hydrogen bonding is a very important effect in infrared spectroscopy. This bonding influences the bond stiffness and so alters the frequency of vibration. For example, for a hydrogen bond in an alcohol, the O–H stretching vibration in a hydrogen-bonded dimer is observed in the 3500–2500 cm−1 range, rather than in the usual 3700–3600 cm^{-1} range.

4. SIMPLE QUANTITATIVE ANALYSIS:

Analysis of Liquid Samples - The quantitative analysis of a component in solution can be successfully carried out given that there is a suitable band in the spectrum of the component of interest. The band chosen for analysis should have a high molar absorptivity, not overlap with other peaks from other components in the mixture or the solvent, be symmetrical, and give a linear calibration plot of absorbance versus concentration.

Analysis of Solid Samples - Simple solid mixtures may also be quantitatively analysed. These are more susceptible to errors because of the scattering of radiation. Such analyses are usually carried out with KBr discs or in mulls. The problem here is the difficulty in measuring the pathlength. However, this measurement becomes unnecessary when an internal standard is used. When using this approach, addition of a constant known amount of an internal standard is made to all samples and calibration standards.

The calibration curve is then obtained by plotting the ratio of the absorbance of the analyte to that of the internal standard, against the concentration of the analyte. The absorbance of the internal standard varies linearly with the sample thickness and thus compensates for this parameter. The discs or mulls must be prepared under exactly the same conditions to avoid intensity changes or shifts in band positions.

CONCLUSION

The ideas fundamental to an understanding of infrared spectroscopy were introduced in this paper. The electromagnetic spectrum was considered in terms of various atomic and molecular processes and classical and quantum ideas were introduced. The vibrations of molecules and how they produce infrared spectra were then examined. The various factors that are responsible for the position and intensity of infrared modes were described. Factors such as combination and overtone bands, Fermi resonance, coupling and vibration–rotation bands can lead to changes in infrared spectra.

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